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Ring opening polymerisation

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In 1932, Carothers reported the thermally induced ring-opening polymerisation (ROP) of trimethylene carbonate [1]. Since then, many ROP processes have been developed, exploiting anionic, cationic, zwitterionic, radical, metathesis and coordination–insertion mechanisms. The varied nature of the mechanistic methodologies has stimulated scientific innovation well-beyond the field of polymer science, bringing together expertise in inorganic and organic chemistry with catalysis, modelling and materials science. ROP has now grown into one of the most powerful polymerisation techniques, giving precise control over polymer molar mass, composition, tacticity and end-group functionality, enabling the synthesis of statistical, (multi-)block and topologically diverse (star-shaped, branched, cyclic) polymers. Beyond academic endeavours, many important commercial polymers are produced via ROP, including Nylon-6 (from ϵ -caprolactam) and polycaprolactone (from ϵ -caprolactone). ROP has also been instrumental in the emergence of renewable polymers such as poly(lactic acid) (PLA) as well as new polymerisation reactions such as the alternating copolymerisation of epoxides and cyclic anhydrides or CO₂. Together these have found application in biomedical, structural, automotive and packaging industries.

This special issue of the European Polymer Journal covers some of the latest developments in ROP, showcasing the vitality of this field of polymer science and its diversity, through twenty-one contributions from all around the world. These key contributions are highlighted below.

Chakraborty and Pappuru [2] have reviewed recent advances in anhydride-epoxide ring-opening copolymerization (ROCOP) using cooperative metal-free Lewis pairs catalysts. In their own review article, Kerton and coworkers [3] provide further specific account of ROP and ROCOP reactions of epoxides catalysed by boron-containing compounds, as well as with species of aluminium and heavier group 13 elements gallium and indium. Until recently, such alternating ring-opening of epoxides has been the preserve of transition metal complexes, such as the ones described in three research articles of this issue. In the first one, Hartweg and Sundermeyer [4] report a series of

quinoline-8-olato chromium(III) complexes with different active (pseudo-)halogen ligands, for the solvent free copolymerisation of carbon dioxide and cyclohexene oxide (CHO), with high activities compared to the state of the art. In a second article, Ko and coworkers [5] have synthesised and fully characterised several dinuclear nickel bis(benzotriazole iminophenolate) catalysts for the same reaction, performing kinetics studies and extending substrate scope to other internal epoxides (cyclopentene oxide and 4-vinyl-1,2-cyclohexene oxide). Finally, Kozak and Anderson [6] report a diethyl dizinc amino-bis(phenolate) complex as an active epoxide ROP and ROCOP catalyst with or without added alcohol co-initiator. They also demonstrated that poly(ether-co-carbonates) from mixtures of epoxides (including renewable limonene oxide) could be synthesized by changes in reaction temperatures and pressures.

The quest for ever faster and more controlled polymerisation reactions, especially under solvent-free conditions of industrial relevance, has been driving the development of new catalysts and initiators for ROP. This thriving area, spanning from organocatalysts to homogeneous metal complexes and heterogeneous clusters, is also well represented in this special issue of EPJ. The ROP of lactide remains the workhorse target for catalyst development due to its combined challenge of stereocontrol and limited ring strain. In the case of the ROP of lactide, the initiator is especially important as it can enable stereoselective polymerisation of this chiral monomer. In their research article, Garden and coworkers [7] report new salen-AlCl complexes featuring meta-NEt₂-substituents, which display high catalyst activities towards rac-lactide ROP with an isotactic bias that suggests a unique activation mechanism. Several contributions also deal with Zn(II) metal complexes as ROP initiators. Herres-Pawlis and coworkers [8] have thus studied some homoleptic zinc Schiff base complexes that can be handled under aerobic conditions, and studied their kinetics by in-situ Raman spectroscopy, revealing competitive rate with industrial standard SnOct₂. Jones and coworkers have dedicated their contribution [9] towards a series of monopyrrolidine metal complexes (including Zn(II) and Zr(IV)), comparing them with previously reported bipyrrrolidine analogues. In the case of Zr complexes opposing stereocontrol was found. In the communication by Thomas and coworkers [10], novel zinc(II) and cobalt(II) complexes containing tripodal mono(phenolate) ligands have been synthesised and tested in the ROP of rac-lactide, with excellent control over molecular weights and dispersities. Other lactones, such as ϵ -caprolactone or δ -valerolactone, are also popular ROP monomers, and several of this special issue articles report catalysts and initiators efficient for these substrates. Continuing with the theme of metal complexes, Ma and Fang [11] disclose the random copolymerisation of lactide and ϵ -caprolactone with zinc complexes bearing pyridyl-based tridentate amino-phenolate ligands. In their research article, Chen and coworkers [12] also studied the ROP of ϵ -caprolactone using novel aluminum complexes bearing 2-(aminomethylene)malonate ligands. A structure-activity study was carried out, which revealed that steric hindrance or electron-withdrawing groups in the ligands increased catalytic activity. Moving away from homogeneous catalysis, Bonnet and workers [13] report novel hybrid poly(lactic acid) by use of a titanium oxo-cluster, acting both as a catalyst and crosslinking agent of the polymer matrix.

Besides metal complexes, organocatalysts has become a powerful tool for polymer synthesis, proposing a genuine alternative to organometallic ROP in terms of activities and control. This special issue of EPJ features two interesting contributions in this area. First, Feng et al. [14] report some novel pyridyl-urea catalysts, which, combined with 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD), showed a fast and living/controlled behaviour in the ROP of ϵ -caprolactone, δ -valerolactone

and trimethylene carbonate. Lia and coworkers [15] also demonstrate in their article the controlled and living ROP of ϵ -caprolactone and δ -valerolactone by means of novel imidodiphosphorimidate catalysts, with cooperative acid/base bifunctionalities.

This special issue also presents how ROP can be applied beyond the aforementioned and well-known lactone monomers, to produce innovative materials with interesting physical properties. In their contribution, Liu and coworkers [16] have for example utilised the ROP of 3-nitratomethyl-3-methyloxetane to produce and characterise a novel energetic propellant polymer binder. Kohsaka et al. [17] report the synthesis of degradable poly(conjugated ester)s by ROP of a cyclic hemiacetal ester bearing an acryl skeleton. ROP proceeds via the elimination of acetaldehyde from the monomer and proposes an alternative to a four-membered lactone ROP. In their contribution, Liu and Hong [18] have exploited polymer transesterification reactions to incorporate γ -butyrolactone (a non-strained 5-membered lactone difficult to copolymerise with high strained lactones), into copolyesters of δ -valerolactone and ϵ -caprolactone with high BL incorporation and high molecular weight, resulting in high melting temperatures. Dove and coworkers [19] derived the structure of lactide and synthesised a novel bis(cyclic diester) crosslinker with flexible linker using thiol-ene chemistry. Using this cross-linker and multi-arm PLA prepolymers provided access to PLA-based thermosets with up to high 268% elongation at break. Flores et al. [20] also used the organocatalysed ROP of lactide to access novel partially biobased ABA triblock copolyesters, from telechelic poly(hexamethylene terephthalate) (PHT) and poly(hexamethylene 2,5-furandicarboxylate) (PHF), demonstrating the influence of the length of PLA blocks on the thermal properties and crystallinity of the resulting materials.

Finally, while this special issue of EPJ has given most of the spotlight to ring-opening transesterification polymerisation (ROTEP) methods, either organocatalysed or initiated by metal complexes, this collection also highlights the use of ring-opening metathesis polymerisation (ROMP) as a powerful ROP tool for material synthesis. In particular, recently, the ROMP of low ring strain monomers (such as cyclopentene) has been an increasing area of interest due to the large variety of functionalised elastomeric materials possible. Kennemur and Guillory [21] have here performed an in-depth study of the ROMP of four different allylic trialkylsiloxy-substituted cyclopentene monomers, and discovered a “Goldilocks” monomer/polymer combination which ensures adequate monomer conversion and high regioregularity in the resulting polymer. Carpentier, Guillaume and coworkers [22] describe in their article the synthesis of new vinylene carbonates which were used to produce α,ω -di(vinylene carbonate) telechelic polyolefins by tandem ROMP and cross-metathesis. These macromolecular dicarbonates were subsequently investigated as precursors for non-isocyanate polyurethanes, via reaction with diamines and model amines.

This themed issue was conceived as a collection of highlights within the fields of ring-opening polymerisation reactions, catalysis and polymers obtained from ROP, with the aim of drawing attention towards new trends and encouraging future discoveries. We thank the authors for their important contributions and hope that this collection will be an inspiration for researchers to further innovate within this stimulating and impactful area of polymer science.

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